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PORT DOCUMENTATION PAGE

AD-A217 748

1b. RESTRICTIVE MARKINGS

3. DISTRIBUTION/AVAILABILITY OF REPORT
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2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)
ARO 23791.2-MS-A

6a. NAME OF PERFORMING ORGANIZATION
DUKE UNIVERSITY

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION
U. S. Army Research Office

6c. ADDRESS (City, State, and ZIP Code)
Department of Mechanical Engineering and Materials Science/Duke University
Durham, NC 27706

7b. ADDRESS (City, State, and ZIP Code)
P. O. Box 12211
Research Triangle Park, NC 27709-2211

8a. NAME OF FUNDING/SPONSORING ORGANIZATION
U. S. Army Research Office

8b. OFFICE SYMBOL (If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
DAAL03-86-G-0046

8c. ADDRESS (City, State, and ZIP Code)
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification) Positron Annihilation Spectroscopy: A Nondestructive, Submicroscopic Characterization Technique for Structural Polymers. (unclassified)

12. PERSONAL AUTHOR(S)
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13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM 9-1-86 TO 8-31-89	1989, November 16	

16. SUPPLEMENTARY NOTATION
The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Positron Annihilation Lifetime Spectroscopy, Polycarbonate, Physical Aging, Structural Relaxation

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Positron annihilation lifetime spectroscopy (PALS) has been used to characterize as extruded and aged LEXAN polycarbonate. The long-lived component of the PALS analysis is attributed to orthoPositronium (oPs) pick off annihilations. The oPs pickoff component lifetime and intensity decrease as the result of the aging heat treatment, and this decrease is associated with a decrease in the free volume site size and concentration in glassy polycarbonate due to aging. Isothermal relaxation experiments performed over the range 12°C to 30°C performed on as-extruded and aged polycarbonate indicate that the relaxation kinetics are significantly different, and are consistent with a decrease in molecular mobility as the result of aging. An activation energy for structural relaxation of 8.2 kcal/mole for aged polycarbonate versus 3.0 kcal/mole for unaged polycarbonate was determined. The relaxation kinetics observed using PALS is related to the structural state and molecular mobility of the polymer.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
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21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL

22b. TELEPHONE (Include Area Code)

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

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UNCLASSIFIED

FINAL REPORT

Proposal Number: 23791-MS
Funding Document: DAAL-86-G-0046

Statement of the Problem Studied

Positron annihilation lifetime spectroscopy (PALS) has been used to study the mechanism of physical aging in polycarbonate. The PALS analysis was supplemented with tensile testing, differential scanning calorimetry, density measurements and x-ray diffraction.

Summary of Findings

The results of this investigation have led to the following conclusions:

1. Physical aging of polycarbonate increases the relaxation times of ortho-positronium (o-Ps) pickoff intensity I_3 during free volume recovery. This increase in relaxation time is a reflection of the increase in molecular response times due to physical aging, which is also evident in the changes in tensile and physical properties (increased yield strength, post yield stress drop, glass transition temperature and density).

2. The time rate of change observed in I_3 during contraction and expansion experiments in glassy polycarbonate is of the same form as volume and enthalpy recovery, and can be modeled similarly.

3. Any change in molecular conformation *during* physical aging is not evident in the o-Ps pickoff lifetime or intensity. Thus, the physical aging phenomena is not the result of a decrease in the amount of free volume or mean free volume cavity size.

4. The physical aging mechanism in polycarbonate is postulated to be associated with either an increase in entanglement density, an increase in the population of *trans* conformations, or a combination of both.

5. Over the temperature range 20°C to 120°C the o-Ps pickoff lifetimes and intensities are lower in aged polycarbonate than in as-

extruded polycarbonate, which is interpreted as a decrease in free volume concentration and cavity size as the *result* of physical aging.

6. The change in I_3 measured during isothermal relaxation experiments for both as-extruded and physically aged polycarbonate can be substituted for the fractional free volume in various theories used to model viscoelastic behavior of glassy polymers.

7. The nondestructive character and relative ease of data collection associated with positron annihilation lifetime spectroscopy could make this technique important in the prediction of physical property response in glassy polymers.

Publications

1. P.L. Jones, A.J. Hill, G.W. Pearsall and J.H. Lind, "A Positron Annihilation Lifetime Study of Poly(Bisphenol-A Carbonate)", Materials Research Society Symposium Proceedings, 82 (1987) 29-34.

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3. A.J. Hill, K.J. Heater and C.M. Agrawal, "The Effects of Physical Aging in Polycarbonate", Journal of Polymer Science, (accepted June 1989).

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